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New Promising Hydride Based on the Cu-Li-Mg System

M H Braga[1,2,3], A Acatrinei[1], M Hartl[1], S Vogel[1], Th Proffen[1] and L Daemen[1]
[1] LANSCE, Los Alamos National Laboratory, mail stop: H805, NM, 87545, USA
[2] CEMUC, Engineering Physics Department, FEUP, Porto University, R. Dr. Roberto Frias, s/n, 4200-465, Porto, Portugal

E-mail: mbraga@lanl.gov

Abstract. We investigated the ternary Cu-Li-Mg system, in particular the $CuLi_xMg_{2-x}$ (x = 0.08) for hydrogen storage. Instead of crystallizing in an orthorhombic phase, as $CuMg_2$, this phase presents a hexagonal structure very similar to that of $NiMg_2$ and $NiMg_2H_{0.3}$. In this work we will discuss the structure of $CuLi_xMg_{2-x}$ by the analysis of the neutron scattering data and first principles calculations. The first results for a hydride (deuteride) phase will also mentioned since preliminary studies at LANSCE showed that $CuLi_xMg_{2-x}$ might absorb approximately 5.3 to 6 wt% of H at an equilibrium pressure of approximately 27 bar at 200 ^oC. If these results are confirmed in future work, this will mean that, not only $CuLi_xMg_{2-x}$ absorbs a considerable amount of hydrogen (close to DOE's expectations for hydrogen storage materials), but also will probably release it at a temperature in the range of 50 to 150 ^oC, where applications are easier to develop. Hence it should be possible to use this alloy with fuel cells or in batteries. Another important observation is that cycling has a strong effect on the structure of the hydride.

1. Introduction

Efficient hydrogen storage remains a major technological obstacle toward the development of a hydrogen-based energy economy. Hydrogen stored as a liquid or gas occupies more space than in a suitable metal hydride or other hydrogen storage materials. Electric and hybrid vehicles already use metal hydrides as the negative electrode (instead of cadmium) in their batteries. In fact, metal hydrides are already being widely used in consumer electronics rechargeable batteries advertised as lasting three times longer than alkaline batteries. In Ni-MH, M is an intermetallic compound. The most common one has the AB_5 type, where A is a rare-earth mixture (e.g., La, Ce, Nd, Pr) and B is Ni, Co, Mn, and/or Al. Note that $LaNi_5H_6$, which is commonly used in batteries, stores only a maximum of 1.4 wt% of H. Another disadvantage of these materials for hydrogen storage is that lanthanides tend to be expensive and heavy.

We are currently investigating the Cu-Li-Mg system. The lighter and cheaper metals and our recent discovery that hydrogen can be reversibly stored in these compounds make it a very attractive alternative to lanthanide-based systems.

$CuMg_2$ has an orthorhombic crystal structure and does not form a hydride: it reacts reversibly with hydrogen to produce Cu_2Mg and MgH_2 [1]. However, $CuLi_xMg_{2-x}$ (x = 0.08) has a hexagonal crystal structure [2] (ICSD database [3]), just like $NiMg_2$, a compound known for its hydrogen storage properties. $NiMg_2$ absorbs up to 3.6 wt% H (of the hydride's weight), at 1 bar and 282 ºC (555 K) [4].

[3] To whom any correspondence should be addressed.

In spite of the fact that the percentage of hydrogen absorbed by $NiMg_2$ is enough to propitiate practical applications, the temperature at which the alloy desorbs hydrogen is much too high for practical applications.

A comparison between the phase diagrams of the systems Cu-Mg and Ni-Mg shows that these binary systems form compounds with similar stoichiometry. $NiMg_2$ is formed by peritectic reaction of the elements at 759 ºC (1032 K) and $CuMg_2$ by congruent melting at 568 ºC (841 K). The presence of Li lowers even further the melting point of $CuMg_2$ [5].

Since the energy of formation of the hydride is related to that of the primary alloy [6], it was hypothesized that $CuLi_xMg_{2-x}$ might also be a hydrogen storage material similar to $NiMg_2$. Presumably, its advantage would be that it would release hydrogen at a lower temperature (possibly close to room temperature) [7].

Preliminary studies at the Los Alamos Neutron Scattering Center (LANSCE) showed that $CuLi_xMg_{2-x}$ might absorb approximately 5.3 wt% H for an equilibrium pressure of approx. 27 bar at 200 ^oC - a pressure and temperature regime easily attainable for practical applications. If these results are confirmed, this will mean that, not only $CuLi_xMg_{2-x}$ absorbs a considerable amount of hydrogen (near the expectations of the US Department of Energy for this type of hydrogen storage materials), but also will probably release it at a temperature in the range of 50 to 150 ^oC, where applications are easier to develop. Hence it should be possible to use this alloy with fuel cells or in batteries and hydrogen storage devices.

2. Sample preparation

The Cu-Li-Mg samples were prepared from the pure elements with a target composition of $CuLi_{0.10}Mg_{1.90}$. They were prepared by mixing stoichiometric amounts of Cu (electrolytic, 99.99% purity, 325 mesh), Mg (99.8% purity, 200 mesh, Alfa Aesar), and small pieces of Li (99% purity, Alfa Aesar). Because of the large vapor pressure of Mg, even below its melting point, the reagents were sealed in a stainless steel crucible in a dry box (He atmosphere). This eliminated possible reagent loss. The samples were heated in a tube furnace with a stirring device to ensure proper mixing of the heterogeneous starting mixture and complete dispersion of Li in the sample. Different reaction temperatures and times were used (from 450 ºC for a day to 1200 ºC for 1-2 h). Regardless of reaction conditions, the samples invariably contained Cu_2Mg, $CuMg_2$, or both. Nonetheless, we obtained final products containing up to 81.0 wt% (75.6 at%) of $CuLi_xMg_{2-x}$. Since the structure of Cu_2Mg and $CuMg_2$ is known, this complication translated merely in the refinement of two additional phases in the neutron powder diffraction pattern.

3. Hydrogen absorption experiments

A sample with 70.1 at% of $CuLi_{0.08}Mg_{2-0.08}$, 22.4 at% of $CuMg_2$ and 7.5 at% of Cu_2Mg was grinded to obtain a powder with particle size of the order of 37 μm. The sample was then studied in a HPVA high pressure absorption analyzer. The latter gas adsorption analyzers are designed to obtain high pressure adsorption isotherms of gases, such as hydrogen, using the static volumetric method. The equilibrium pressure of hydrogen versus the ratio between the number of atoms of H and the number of atoms of the other elements present in the $CuLi_{0.08}Mg_{2-0.08}$ was plotted in figure 1 a). It was also plotted in figure 1 b) the equilibrium pressure of hydrogen versus the ratio between the weight percentage of H and the weight percentage of H + $CuLi_{0.08}Mg_{2-0.08}$. Results show an isothermal curve that is much different of those obtained by Reilly and Wiswall for $NiMg_2$ [8] and $CuMg_2$ [1]. Even at a lower temperature, the difference between plateau pressures is higher than 21 atm. The latter mean that $CuLi_{0.08}Mg_{2-0.08}$ will release hydrogen at a much lower temperature. On the other hand, it seems that $CuLi_{0.08}Mg_{2-0.08}$ will absorb hydrogen corresponding to the formation of a hydride with $H/(Cu+Li+Mg) > 1.33$ (probably equal to 2 or higher).

4. Neutron scattering in deuteride and hydride samples

Time-of-flight (TOF) neutron diffraction data were collected at low and room temperatures on

NPDF and at room and high temperatures at HIPPO neutron diffractometers at LANSCE.

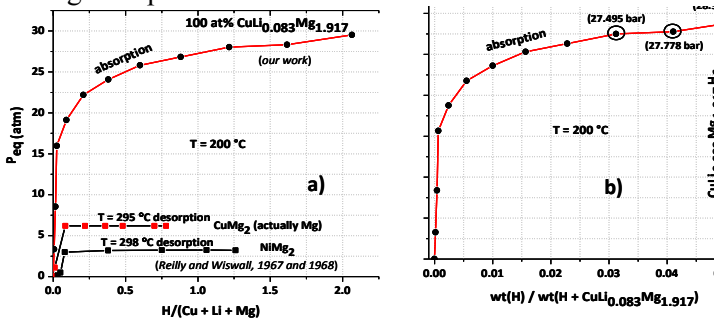

Figure 1. Absorption isothermal (at 200 °C). Equilibrium pressure of H as a function of: a) atoms of H/(Cu + Li + Mg) b) wt(H)/wt(H + $CuLi_{0.08}Mg_{1.92}$). It was considered that at 200 °C only $CuLi_{0.08}Mg_{2-0.08}$ will absorb hydrogen, since $CuMg_2$ will only start absorbing hydrogen at T ≥ 270 °C and Cu_2Mg at an even higher temperature.

5. Neutron scattering in deuteride and hydride samples

Time-of-flight (TOF) neutron diffraction data were collected at low and room temperatures on NPDF and at room and high temperatures at HIPPO neutron diffractometers at LANSCE.

5.1. Neutron diffraction

Neutron diffraction was firstly performed in order to characterize the phase $CuLi_xMg_{2-x}$. Rietveld refinements using GSAS [9] and Pair Distribution Function (PDF) refinements using PDFgui [10] were performed to characterize the phases present in the samples.

Two different measurements of the samples are shown in figure 2 and 3 for two different temperatures.

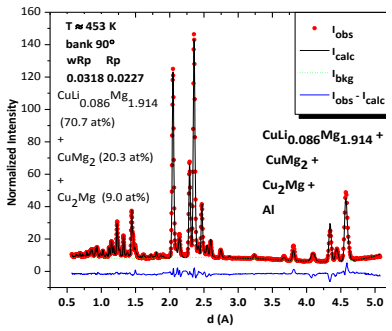

Figure 2. Refined neutron diffraction at T = 453 K. The sample contained $CuLi_{0.08}Mg_{1.92}$, $CuMg_2$ and Cu_2Mg; sample holder was of Al and the measurements were done on HIPPO.

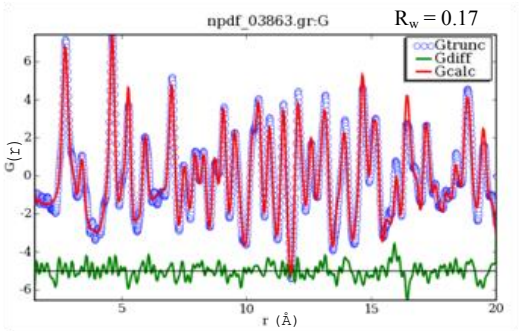

Figure 3. PDF fit after a NPDF measurement at T = 150 K. Sample containing $CuLi_{0.08}Mg_{1.92}$, $CuMg_2$ and Cu_2Mg.

Results obtained show that Li will substitute Mg in (1/2, 0, z) forming a hexagonal $P6_222$ compound $CuLi_{0.08}Mg_{1.92}$ with lattice parameters, a = b = 5.250 (1) Å and c = 13.621(1) Å (at T = 300 K).

5.2. Inelastic neutron scattering

A sample with 75.6 at% of $CuLi_{0.08}Mg_{1.92}$ and 24.4 at % of Cu_2Mg was loaded with H_2 at 200 °C and at different pressures and loading times of the order of several hours, before collecting a neutron vibrational spectrum (treatments were done on the same sample after each measurement). The sample was loaded:

- under 515 psi of H_2 pressure for 1 hour once (yellow curve),
- twice under 1450 psi of H_2 for 6 hours and once for 21 h (green curve),
- once for 17 h and 25 min. and twice for 3 hours (blue curve).

All data were collected at 10 K.

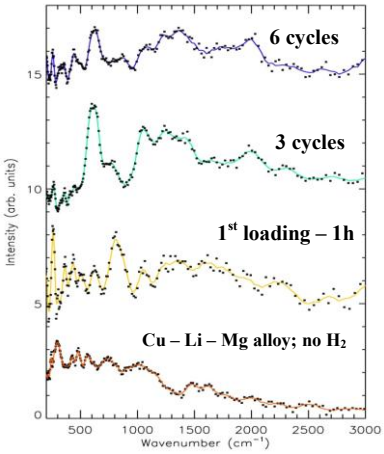

Figure 4. Inelastic neutron scattering (INS) results after cycling a sample with 75.6 at% of $CuLi_{0.08}Mg_{1.92}$ and 24.4 at % of Cu_2Mg with H_2.

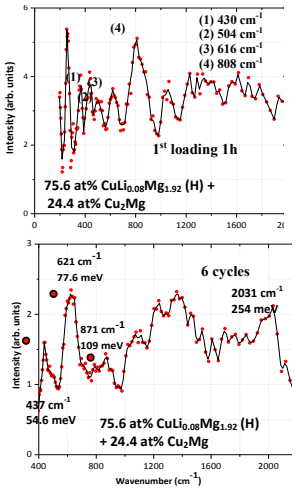

Figure 5. INS results for two different structures of the $CuLi_{0.08}Mg_{1.92}H_z$ hydride. Results show different structures depending on the number of cycles.

INS results show that cycling has a strong effect on structure and ion distribution. These results show that during the first loading the structure was monoclinic with the Cu (bonded to H) ion occupying C_1 sites like $[NiH_4]^{4-}$ ion in $NiMg_2H_4$ (monoclinic) [11], and after 6 cycles tetragonal with Cu (bonded to H) ion occupying C_{4v} sites like $[CoH_5]^{4-}$ ion in $CoMg_2H_5$ (tetragonal) [12].

Summary

This work presents a new compound, never studied before as a hydrogen storage material. In future work more absorption/desorption experiments will be done as well as neutron diffraction experiments, after deuterium absorption, to determine the structure of the hydride/deuteride phase. It is also possible that, as in the case of $CuMg_2$, MgH_2 will be formed upon hydrogen absorption.

Acknowledgments

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6. References

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